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P. O. BOX 13400 SACRAMENTO, CALIFORNIA 95813 • A DIVISION OF AEROJET-GENERAL 

STUDY OF THE THERMAL DEGRADATION MECHANISM  
OF A COMPOSITE PROPELLANT

1196-81F

FINAL REPORT

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### ABSTRACT

The current experimental program was designed to systematically investigate the role of the oxidizer in the thermal degradation process of composite propellants. The primary analytic tool was the scanning electron microscope (SEM) which was used to examine the failure sites in thermally degraded propellant samples. The formulation variables tested were oxidizer purity, oxidizer particle size and oxidizer to binder bonding agent. The binder, a saturated hydrocarbon, was kept constant throughout the experiments. The oxidizers were: AP, chlorate-doped AP, arsenate-doped AP and phosphate-doped AP. The oxidizer particle size distribution was 60% of the large fraction and 40% of the small fraction. The two blends used were: 125-175 $\mu$ / $<44\mu$  and 175-250 $\mu$ /44-88 $\mu$ . Finally, the bonding agent, when present, was used at the 0.15% level. The test variables were temperature, 100, 135 and 170°C, and stress 0, 4.1 and 8.7 psi. The data showed that both the oxidizer purity and particle size had an important affect on the thermal degradation process. The affect of the oxidizer particle size was more noticeable at the higher temperature and stress levels. An examination of the failure site, by SEM, of propellants subject to these latter conditions indicated that the fracturing of the large oxidizer particles led to the propellant cracking.

## I. INTRODUCTION AND SUMMARY

All composite propellants are known to age, that is, some of their physical properties change with time. This aging may be due to a change in one of the constituents, e.g., plasticizer migration, the interaction of several components, e.g., oxidizer-fuel reaction or the reaction of a component with the environment, e.g., surface air oxidation. All of these problems tend to be aggravated at higher temperatures. They are therefore of particular concern to the NASA sterilizable motor program where a composite propellant is subjected to temperatures as high as 135°C for extended time periods.<sup>(1)</sup>

While significant progress has been made in producing motors which can be heat sterilized the mechanism by which the propellant degrades is not yet fully understood. This limits the planners ability to predict what will occur if (1) the temperature requirement is altered for a given formulation, (2) the grain geometry is altered, or (3) the formulation has to be altered to meet a new requirement such as a lower burning rate.

Previous experimental work has demonstrated the critical role of the oxidizer (and minor alterations therein) on the degradation process.<sup>(2-5)</sup> The current program was designed to systematically investigate the role of the oxidizer in the thermal decomposition of composite propellants. The primary analytic tool was the scanning electron microscope (SEM) which was used to examine the failure sites in thermally degraded propellant samples. Temperature and stress were the experimental conditions which were varied. The range of the test variables investigated was chosen so as to bracket the conditions to which a heat sterilized motor might be subject. Three temperatures, 100°C, 135°C and 170°C were selected for the experiments. Additionally, the thermally aging composites were subject to three stress levels, 0, 4.1 and 8.7 psi at each of these three temperatures.

The formulation variables tested were oxidizer purity, oxidizer particle size and oxidizer to binder bonding agent. The binder, a saturated hydrocarbon, was kept constant throughout the experiments. The oxidizers were: AP, chlorate-doped AP, arsenate-doped AP and phosphate-doped AP. The oxidizer particle size distribution was 60% of the large fraction and 40% of the small fraction. The two blends used were: 125-175 $\mu$ / $<44\mu$  and 175-250 $\mu$ /44-88 $\mu$ . Finally the bonding agent, when present, was used at the 0.15% level.

The data showed that not only oxidizer purity but also oxidizer particle size has an important affect on the thermal degradation process. The chlorate-doped AP always gave the least stable composite while the phosphate-doped composites were thermally the most stable. At the higher temperature (170°C) and stress levels, AP particle size became very important in determining when a composite would fail. As noted, the time-to-failure of chlorate-doped composites was always less than comparable phosphate-doped propellants. However, by reducing the large particle size fraction in a chlorate-doped composite from 212 $\mu$  to 150 $\mu$  it became more stable than the 212 $\mu$  phosphate-doped composite.

The data also indicate that thermally aging propellant samples under stress is a method which, through some refinement, can be used as a tool to predict the performance of propellants on sterilization in a motor. The results also indicate such testing should be performed near the motor sterilization temperatures as the nature of the mechanism which leads to failure is a function of temperature, i.e., any extrapolations over  $\sim 20^\circ\text{C}$  may be in error.

## II. EXPERIMENTAL

### A. EQUIPMENT

The basic instrument used in the infrared (IR) spectroscopic studies is the Beckman IR-9. All differential thermal analyses (DTA) are performed with a duPont 900 DTA. Non-isothermal thermogravimetric analyses are performed with an attachment to the duPont 900 (TGA 950). Isothermal decompositions are run on an Ainsworth automatic recording balance using a Honeywell temperature controller. Temperature control at 300°C is  $\pm 2^\circ\text{C}$ . The sample temperature is measured by a Pt-Pt-10% Rh thermocouple located immediately below the sample holder.

Scanning electron microscopy is performed with a Cambridge Mark 2A SEM located at the University of California at Davis. A Polaroid camera attachment is used to record the scan.

### B. SAMPLES

#### 1. Oxidizer

##### a. Recrystallized $\text{NH}_4\text{ClO}_4$

All experiments are being performed with a single lot of ammonium perchlorate (AP). The AP has been recrystallized twice from an aqueous solution that is kept at a pH of  $\sim 7-8$  by the addition of small amounts of  $\text{NH}_4\text{OH}$ . This AP is dried for 48 hours under

vacuum at 50°C. It is used in all control experiments and serves as the starting material for any doped AP that is required.

b. AP Containing Chlorate

The required amount of AP is dissolved in water at ~60°C. The desired amount of  $\text{KClO}_3$  is then added and the solution taken to dryness under vacuum at ~50°C. Chlorate is analyzed for by the method of Chen.<sup>(6)</sup> This is a spectrophotometric method in which ferrous ion is used as a reducing agent. The quantity of ferric ion produced is measured in a sulfuric acid medium at 300m $\mu$ .

c. AP Containing Phosphate

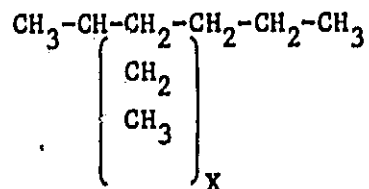
The following is the procedure used in the preparation of AP containing a small percentage of phosphate. In this report phosphate is taken to mean the sum of  $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$ , and  $\text{PO}_4^{3-}$  since the exact form in the crystal is not known. Dissolve AP in water at ~60°C (AP to  $\text{H}_2\text{O}$  ~ 1:2). Add  $(\text{NH}_4)_2\text{HPO}_4$  and continue stirring until all salts are dissolved. The temperature is kept below 65°C. The solution is then cooled to ~5°C in an ice bath and filtered. The crystals are dried in a vacuum oven at 50°C for 72 hours. Phosphate is analyzed for by the method of Gee and Deitz.<sup>(7)</sup> It was experimentally determined that the AP did not affect this method of analysis. The method is a spectrophotometric one utilizing a mixed molybdate metavanadate solution to develop the color. Measurements are made in the region of 350-400m $\mu$ . The analysis is sensitive to the acid concentration which must be reproducibly controlled.

d. AP Containing Arsenate

$\text{As}_2\text{O}_5$  is dissolved in water to form arsenic acid,  $\text{H}_3\text{AsO}_4$ . The pH of the solution is then adjusted with  $\text{NH}_4\text{OH}$  such that the dominant arsenic containing species are  $\text{H}_2\text{AsO}_4^-$  and  $\text{HAsO}_4^{2-}$ . The procedure for making arsenic doped AP is essentially the same as that described for doping the AP with phosphate. Arsenic is analyzed for by first reducing it to arsine,  $\text{AsH}_3$ , with zinc in acid solution. The arsine is then passed into a pyridine solution of silver diethyldithiocarbamate. The arsenic reacts with the silver salt forming a soluble red complex which is measured photometrically at 530m $\mu$ .<sup>(8)</sup> The percentage of arsenate reported is taken to be the sum of  $\text{H}_2\text{AsO}_4^-$ ,  $\text{HAsO}_4^{2-}$  and  $\text{AsO}_4^{3-}$  since the form of the anion in the crystal is not known.

## 2. Prepolymer

The saturated prepolymer used was one from General Tire and Rubber (Telagen) which is the prepolymer used in the NASA sterilizable motor program.



X ~ 20 mole % of carbon is in the side chains.

This material was obtained from the sterilizable motor program<sup>(1)</sup> where it had been stripped, i.e., two passes through a wipe film column at ~200°C.

## 3. Propellants

### a. Base Formulation

The basic formulation is that of the propellant, ANB-3438, developed in the heat sterilizable motor program.

<u>Ingredient</u>	<u>wt%</u>	<u>No. of Equivalents</u>
NH <sub>4</sub> ClO <sub>4</sub>		
Large particle size	39.6	
Small particle size	26.4	
Al (H-5)	18.0	
Binder		
Telagen S	11.104	58
GTRO (Glycerol triricinoleate)	2.637	42
IPDI (Isophorone diisocyanate)	2.109	105
Bonding Agent*		
FC-217	0.15	

\* Not used in all formulations



b. Formulation Variables

The formulation variables are all related to the oxidizer. They are:

- oxidizer purity
- oxidizer particle size
- oxidizer-binder bonding agent.

The basic oxidizer used in all of the experiments was  $\text{NH}_4\text{ClO}_4$ . However, the AP thermal stability was altered through the use of dopants which were selected, on the basis of previous experiments, to both accelerate and decelerate its decomposition. The desired particle sizes were obtained by grinding the AP in a mortar and then screening this material. To reduce the total number of tests only the chlorate and phosphate doped AP was used with the smaller particle size formulations. However, these materials served to bracket the range of oxidizer thermal stability. There were six basic formulations which were repeated with the addition of a bonding agent. The formulation test matrix is given in Table 1.

c. Thermal Aging

(1) Sample Preparation

After the propellant samples were cured at 135°F for 8 days they were cut into small bars with a cross section of  $\sim 1.2 \times 1.2$  cm. There was insufficient propellant to cut the desired number of standard Instron bars out of the one-pound mixes therefore the smaller bars were used for these tests. The ends of the bars were attached to metal hooks with an epoxy, Shell 901.

The first experiments showed that at 135°C and above, the sample strand broke at the epoxy joint. They did not pull away from the end holder but rather the propellant appeared to break due to a reaction with the epoxy. A small Instron shaped bar was cut next, using a cutter built for the occasion, and the ends were attached to the propellant with a combination of wrapped wire and epoxy.

(2) Thermal Environment

The samples were placed in three, 100°C, 135°C and 170°C closed circulation ovens. Sample strands were hung from a rack near the center of the oven and in close proximity to the controlling

TABLE 1

IDENTIFICATION OF FORMULATION VARIABLES BY NAS1-xxxx  
MIX NUMBER

Oxidizer			
Large Fraction - 175-250 $\mu$ 39.6%			
Small Fraction - 43-88 $\mu$ 26.4%			
AP	AP/PO <sub>4</sub> (0.08%)	AP/ClO <sub>3</sub> (0.01%)	AP/AsO <sub>4</sub> (0.14%)
2850*	2851*	2852*	2913*
2855	2908	2909	2910
Large Fraction - 125-175 $\mu$ 39.6%			
Small Fraction - <44 $\mu$ 26.4%			
	AP/PO <sub>4</sub> (0.08%)	AP/ClO <sub>3</sub> (0.01%)	
	2853*	2854*	
	2911	2912	

\* 0.15% bonding agent

thermocouple. The temperature was recorded on a strip chart which showed a temperature cycle of  $\pm 2^{\circ}\text{C}$  at  $100^{\circ}\text{C}$  and  $\pm 3^{\circ}\text{C}$  at  $135^{\circ}\text{C}$  and  $170^{\circ}\text{F}$ , except for those times the ovens were opened to check the samples. These times were kept short relative to the overall time the sample was in the oven.

The stress levels were obtained by hanging lead weights from the bottom of the strands. These weights were made (poured into a cone shape) so that the stress was below 5 psi for one third of the samples and greater than 5 psi for another third. The remaining one third were not subject to a stress during heating.

#### d. SEM Analysis

##### (1) Sample Preparation

When a sample bar broke in the oven it was removed as soon as possible to prevent further reaction at the break surface. This surface was sliced from the strand and mounted on an SEM button. Initially when a strand did not break during the time of the test (20 days) a section was cut out of it for analysis. It was noticed that in this procedure the larger AP crystals inevitably become fractured. Later samples, that did not break under the thermal aging conditions, were therefore pulled on the Instron machine and this break surface used for analysis.

##### (2) Analysis

The samples were scanned, at low magnification (20X to 100X), in search of features which would help explain the thermal decomposition mechanism of these propellants. Unusual features were magnified to the appropriate level and photographed. It was often difficult to interpret such areas as the binder oxidizer interface from the two dimensional picture. Therefore, some "duplicate" shots were made separately by approximately a 7 to 8° rotation. These pictures, when viewed on a stereo viewer, offered a far more comprehensive picture of the propellant surface than is available from the two dimensional view.

### III. RESULTS

#### A. TEST VARIABLES

##### 1. Temperature

The experiments were run at three temperatures,  $100^{\circ}\text{C}$  ( $212^{\circ}\text{F}$ ),  $135^{\circ}\text{C}$  ( $275^{\circ}\text{F}$ ) and  $170^{\circ}\text{C}$  ( $338^{\circ}\text{F}$ ). The upper end of this temperature range is significantly above those temperatures currently projected for sterilization of NASA space vehicles. The results were not linear with

temperature such that a propellant may show relatively good stability at the lower temperatures, e.g., arsenate doped oxidizer, but relatively very poor stability at the higher temperature. In this particular case it is believed the problem is due to the thermal decomposition of the ammonium arsenate salts at the higher temperatures. At the 170°C temperature all samples under stress broke and all others cracked in relatively short times. While experiments at these temperatures did discriminate the best from the poorest samples the selectivity at the intermediate points was not as good as desired.

## 2. Stress Level

The stresses, based on a cross section of 1.4 cm<sup>2</sup> at the narrowest section of the strand, were 0 psi, 4.1 psi and 8.7 psi. As noted above at 170°C all samples at 4.1 and 8.7 psi stress broke during heating. At 100°C only a few samples broke under a stress of 8.7 psi. In the intermediate range of 135°C some samples broke at both of these stress levels. At 170°C the 8.7 psi stress load was too high to give reliable data on the quality of the strands, however, the 4.1 psi stress level appeared to be reasonable for this temperature. At the intermediate temperature, that closest to the one used for the sterilizable motor, either stress level was satisfactory if sufficient time was available. At the 100°C temperature even the 8.7 psi stress caused only the poorest sample to break during the time (~500 hours) of these experiments.

## B. FORMULATION VARIABLES

### 1. Oxidizer Purity

Due to the nature of these experiments, i.e., approximate cross sectional area of strands, reaction at epoxy propellant interface, etc., the time until a sample broke in these experiments can only be taken as an approximation of its thermal stability. However, even under these conditions the importance of the oxidizer "purity" is very evident as can be noted from the following data, Table 2, obtained with non-bonded propellant samples.

TABLE 2

TIME TO BREAK AT TWO STRESS LEVELS AND THREE TEMPERATURES

<u>No.</u>	<u>Oxidizer</u>	<u>Temperature, °C</u>	<u>4.1 psi, hrs.</u>	<u>8.7 psi, hrs.</u>
2909	AP · ClO <sub>3</sub>	170	4	<0.5
2855	AP	170	10	1.5
2908	AP · PO <sub>4</sub>	170	14	2.0
2909	AP · ClO <sub>3</sub>	135	(a)	3
2855	AP	135	(a)	(a)
2098	AP · PO <sub>4</sub>	135	(a)	(a)
2909	AP · ClO <sub>3</sub>	100	(a)	170

(a) Did not break during the 500 hr. test.

2. Particle Size

While it was proposed that oxidizer particle size might have an effect on the thermal stability of the propellants the magnitude of this effect was underestimated, at least at 170°C, Table 3.

TABLE 3

STRAND INTEGRITY<sup>(a)</sup> AS A FUNCTION OF OXIDIZER  
PARTICLE SIZE AT 170°C

<u>AP Particle Size, μ</u>		<u>AP · ClO<sub>3</sub> hrs.</u>	<u>AP · PO<sub>4</sub> hrs.</u>
60%	40%		
175-	43-		
250	88	<0.5	2.0
125-	<44		
175		5.5	14.0

(a) at 8.7 psi

### 3. Bonding Agent

The effect of the bonding agent is not definitive. This is partially due to the break failures in the more stable samples occurring at the previously mentioned epoxy interface. Some of the pertinent data are given in Table 4.

TABLE 4

#### EFFECT OF BONDING AGENT ON STRAND INTEGRITY AT 170°C

AP Particle Size <u>μ</u>		Bonding Agent 0.15%	AP · ClO <sub>3</sub>		AP · PO <sub>4</sub>	
			4.1 psi hrs.	8.7 psi hrs.	4.1 psi hrs.	8.7 psi hrs.
175- 250	43- 88	Yes	4.0	1.5	(a)	(a)
175- 250	43- 88	No	4.0	<0.5	14	2
125- 175	<44	Yes	14	(a)	36 (b)	(a)
125- 175	<44	No	(a)	5.5	32 (b)	14 (b)

(a) Data not usable.

(b) Broke at epoxy.

### IV. DISCUSSION

The current experimental program is based on the results obtained under previous NASA sponsored programs. Therefore, a brief review of pertinent data generated during these previous NASA sponsored programs is included in the current discussion.

An examination of AP particles that have been heated shows, that at a given time, some crystals are partially decomposed while others with the same thermal history do not show any signs of decomposition. Therefore, while the overall rate of decomposition may be reproducible it is based on a statistical distribution among the individual particles. An examination of heat cycled motors has shown a similar effect even when the AP is in a polymeric matrix. That is, the decomposition begins with specific AP particles and the reaction then propagates by interface reaction between the binder and the initial AP decomposition products. The phenomena of decomposition originating at specific AP particles in a propellant matrix has also been noted in studies at JPL.(9)

There is thus a strong indication that the initial step in the propellant degradation is a function of the oxidizer. If in fact it were some heterogeneous AP polymer reaction it could be expected that the effect would be general at all the oxidizer-polymer interfaces. If the initiation of the decomposition is a function only of the oxidizer it must occur even when there is no organic fuel present. However, under similar time-temperature conditions the AP is considered to be stable (weight loss or pressure measurements). These apparently contradictory data can be reconciled if the initial decomposition occurs on the surface of the AP but the products of this dissociation remain on the surface in equilibrium with the  $\text{NH}_4\text{ClO}_4$ . The binder functions by reacting with these products, driving the dissociation forward, and thereby propagating the overall decomposition reaction.

Since the initial step in the overall degradation of the composite is the decomposition of the oxidizer the purity of the oxidizer can be expected to influence the thermal stability of an AP composite propellant. Important to the current study is the effect of both positive and negative catalytic dopants on the thermal stability of  $\text{NH}_4\text{ClO}_4$ . Thus it is important to summarize some earlier data:

- (a) Catalytic impurities such as  $\text{ClO}_3^-$  accelerate the degradation mechanism.
- (b) Pure AP is only moderately thermally stable when mixed with a fuel component.
- (c) Negative catalytic anions such as arsenate and phosphate result in a significant increase in the thermal stability of AP composites.

#### A. OXIDIZER PURITY

The current study has reaffirmed the fact that the prime requirement for making a thermally stable composite propellant is the use of thermally stable AP.

These data have shown the marked catalytic effect of chlorate ion on the decomposition of AP and therefore the degradation of propellants containing this AP. An examination of the SEM pictures gives direct evidence of the thermal instability of chlorate doped AP. What really distinguishes this material from pure AP is that decomposition appears to be initiated over the entire surface of the crystal and propagate through the crystal, Figures 1-4. In contrast, the decomposition of "pure" AP is initiated at specific points on the surface and then gradually propagates from these sites.

It is clear that even if the products of the oxidizer decomposition did not react with the binder components the propellant would be weakened by:

- (1) the residual skelton AP structure, Figures 5 and 6.
- (2) the pressure generated by the volatile products given off during the oxidizer decomposition.

The extent of oxidizer binder reactions appears to be a function of the temperature. That is, at the lower temperatures (longer time periods) the binder decomposition is different than at the higher temperatures. At 170°C there is evidence of the binder melting, Figures 1, 7 and 8, i.e., crosslink breakdown, while at the lower temperatures there is an increase in the brittleness of the propellant due to an increase in crosslinking (the probable radical mechanism for this reaction is discussed in Reference 5). Therefore, the nature of the propellant failure mechanism may also be a function of the temperature.

Stabilizing dopants such as phosphate do not appear to change the nature of the AP decomposition process, as does chlorate, they simply repress the rate of the decomposition mechanism. This occurs primarily through a slowing down of the rate of formation of decomposition sites on the AP surface. In the case of AP, which has been negatively catalyzed with phosphate, decomposition is initiated at specific sites on the surface and propagates from these sites, Figures 9 and 10. From these SEM pictures it can be seen that this method of decomposition does not weaken the AP crystal to the extent that occurs with the chlorate propagation mechanism, e.g., where the entire crystal becomes porous. Figure 11 shows, through highly magnified SEM pictures, the spread of decomposition along the surface of negatively catalyzed AP crystals. Figure 12 shows a comparison between a chlorate doped AP crystal and a "pure" AP crystal in propellants which have been subjected to 100°C for ~500 hours. The high magnification picture (~10K) of the non-doped AP crystal shows areas, ~0.5 x 2.0μ which could represent initiation sites.



Figure 13 shows that AP crystals which have "point" decomposition initiation sites can occur in propellants containing chlorated AP. There are several possible explanations but the simplest, and most probable, is that chlorate ion does not become incorporated in every AP crystal in the chlorate doped AP preparation. The converse situation, i.e., porous crystal decomposition in pure AP or negatively catalyzed AP propellants was not observed during these experiments.

Since overall propellant degradation is initiated at sites on the oxidizer surface the overall propellant thermal stability is inversely related to the rate of oxidizer decomposition site formation.

#### B. OXIDIZER PARTICLE SIZE

The oxidizer particle size turns out to be an important factor in determining the thermal stability of an AP propellant. The effect is related to what appears to be the preferential (for a given time - temperature history) decomposition of the larger crystals over the smaller AP crystals. At this time there is insufficient data to define large and small but for this discussion, large will be used for those particles over  $\sim 125\mu$  and small for those under  $\sim 80\mu$ . In all of the SEM pictures studied when there was evidence for AP decomposition it was the large rather than the small oxidizer crystals which were decomposing. This is most likely related to defects in the less than perfectly grown crystal. When the crystal is ground to produce the smaller particle size fraction oxidizer the crystal may well break along these imperfections resulting in smaller particles which have less imperfections than the original crystal. This interpretation would indicate there is no relationship between particle size and stability per se but rather a practical relationship since it is very difficult to form large perfect crystals.

This relationship between AP particle size and propellant integrity is a function of stress, a factor which must be taken into consideration in all real motors. Once a large crystal has started to decompose it becomes structurally weak. The evidence from the current study shows that at some point, if the propellant is under stress, the crystal itself rather than the crystal-binder interface or the binder becomes the weak point in the propellant. The crystal generally does not pull loose from the binder but breaks along a cleavage plane, Figures 14-16. Therefore the stability is related to the cross sectional area of these large crystals and would not be expected to be linear with particle diameter. While there are only

two points available from the current study it can be seen that the change from a 150 $\mu$  fraction to a 212 $\mu$  large particle size fraction significantly reduces the stability of the propellant under stress. In this case while the increase in diameter from 150 $\mu$  to 212 $\mu$  is only ~40% the increase in area is ~100%.

### C. BONDING AGENT

The effect of the bonding agent on thermal stability is a function of the oxidizer purity, the temperature and the stress level. That is a propellant with an oxidizer such as chlorated AP at a high temperature and under stress will fail with or without a bonding agent. Under these conditions the large AP crystals tend to fracture rather than pull out of the polymeric matrix. Data from a motor program (Reference 1) has shown that the bonding agent is a factor in determining thermal stability. Why a bonding agent has an affect at the more moderate temperatures (up to 135°C) and stress levels encountered in the motor program is not yet understood. The data from the current program, on this variable, are too erratic to shed any light on the role of the bonding agent in determining thermal stability. Figure 17 shows a propellant containing a bonding agent before heating and after having been subjected to 135° temperatures. It can be seen that initially the polymeric matrix adheres strongly to all the particles present. After heating there is a definite gap separating the large AP particles from the polymeric matrix. As noted earlier although this was seen often in the case of the large AP particles it, separation from the binder, was rare for AP particles <80 $\mu$ .

The bonding agent could either affect the initial decomposition reaction, the secondary propagation reaction or the physical integrity of the oxidizer-polymer interface. Since most bonding agents (aziridines) have a basic nitrogen they may affect the surface migration of perchloric acid in much the same way as do the phosphate additives. It is more difficult to speculate on their effect on the propagation reaction. If their reaction with the original oxidant radicals resulted in a trapping effect, i.e., not propagating to the main polymeric backbone, this could stabilize the propellant. Additional experiments are needed to clarify the mechanism by which the bonding agent affects the thermal stability of a composite propellant.

#### IV. CONCLUSIONS

A. The quality of the AP is of primary importance to the thermal stability of an AP-composite propellant.

1. It must be free of catalytic impurities such as chlorate ion.

2. It must contain small amounts of negative catalysts such as phosphate ion.

B. The particle size of the oxidizer can affect the integrity of the propellant at sterilization temperatures.

1. The larger the AP crystal the more likely it is to fracture under stress. The relationship between particle diameter and structural integrity is not linear but appears to follow a power law, or be better related to the cross sectional area of the particle.

2. The higher the temperature and the higher the stress level the more important does the oxidizer particle size become in determining thermal stability.

C. Bonding agents can improve the stability of heat sterilized propellants, however, their effectiveness is related to the oxidizer purity, particle size, temperature and stress. They are most beneficial in improving an otherwise good propellant, e.g., stable oxidizer, moderate particle size, under moderate stresses and temperatures. However, they appear to do little to improve "poor" heat sterilizable propellant.

D. It is believed that by adding stress to small samples, subject to an elevated thermal environment, it is possible to make this small scale procedure into a predictive tool for motor performance.

#### V. RECOMMENDATIONS

##### A. PARTICLE SIZE

A more complete determination of the effect of oxidizer particle size on thermal stability. Four bimodal blend propellants should be made using a single type of oxidizer. The large particle size fraction should be varied from an average of  $\sim 125\mu$  to  $\sim 300\mu$ .

##### B. BONDING AGENT

Two bonding agents of significantly different basicities should be used to investigate their role in the decomposition mechanism.

This should be done as a function of both temperature and stress.

C. PREDICTIVE TOOL FOR DETERMINING THERMAL STABILITY OF A PROPELLANT

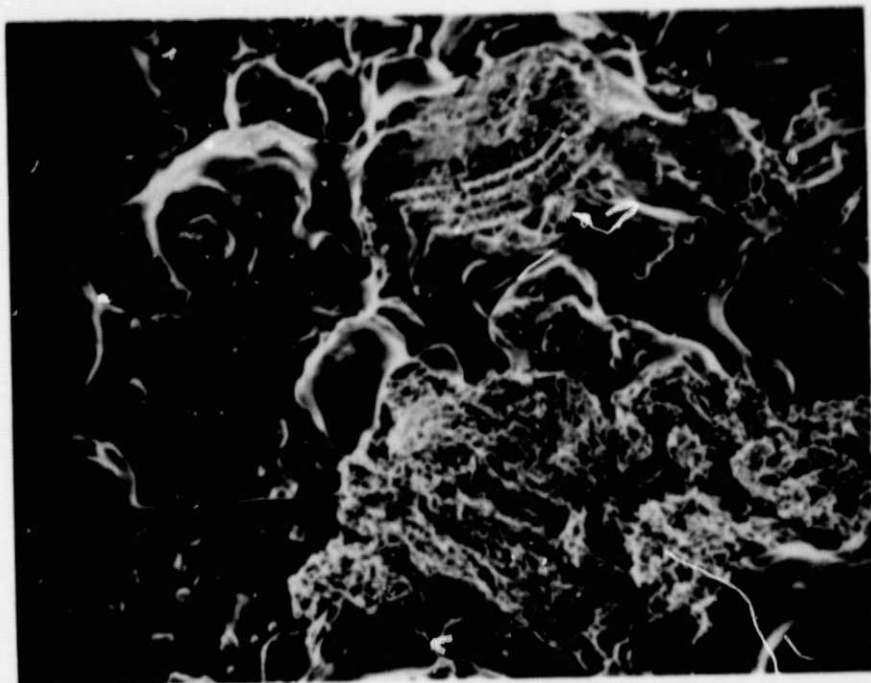
Measurements such as time to fracture, or force needed to break, a strand at elevated temperatures, under stress, should be repeated. However, the experimental condition and instrumentation should be more precise than in the current experiments. That is, the strands cross section should be closely controlled as should the stress levels. Improvements should be made on attaching the strand end pieces as well as automatic recording of the break time (if that is the approach to be used). The last factor is that the measurements be made within  $\pm 20^{\circ}\text{C}$  of the temperature to be used in the motor for which the prediction is desired.

D. ESTABLISH A DEFINITION FOR FAILURE

That is, at what level of decomposition are the ballistic and/or physical properties of the propellant altered to the point where the motors' mission will be impaired.

# REFERENCES

1. Sterilizable Motor Demonstration Program, NAS1-10861.
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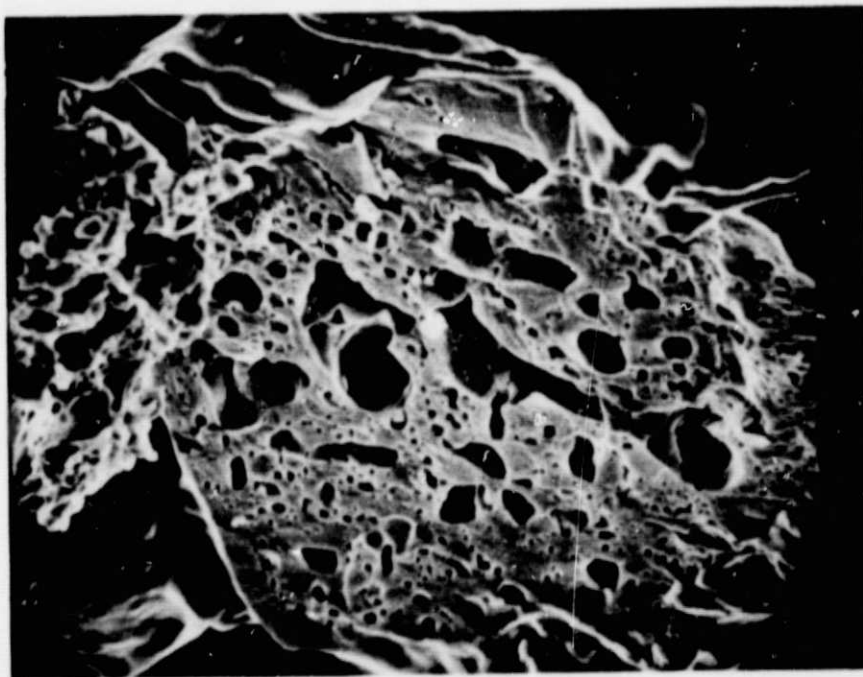
X 238

1 cm ~50μ

NAS1-2854

170°C

0 Stress



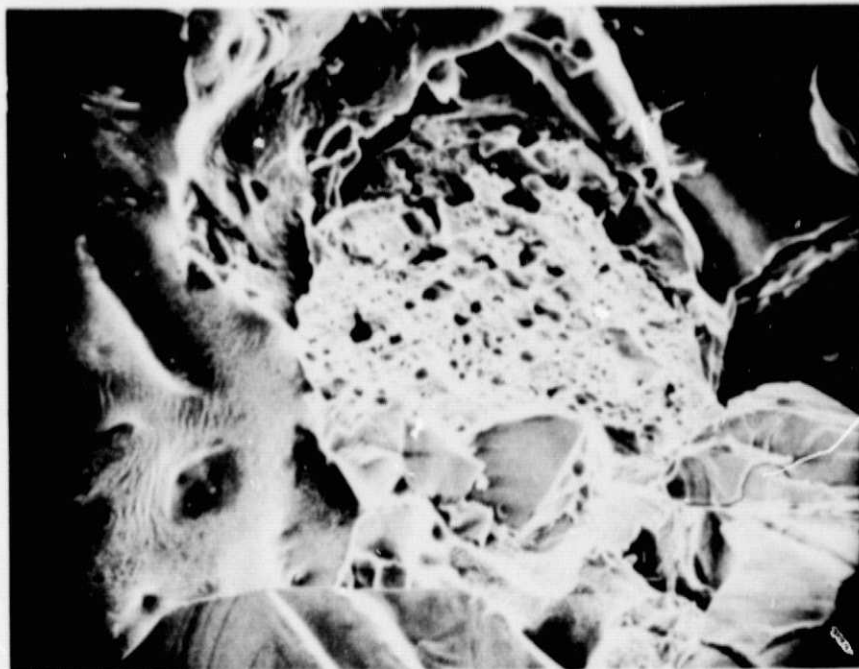
X 1.1K

1 cm ~10μ

NAS1-2852

170°C

0 Stress



X 490

1 cm ~20μ

NAS1-2852

135°C

4.1 psi



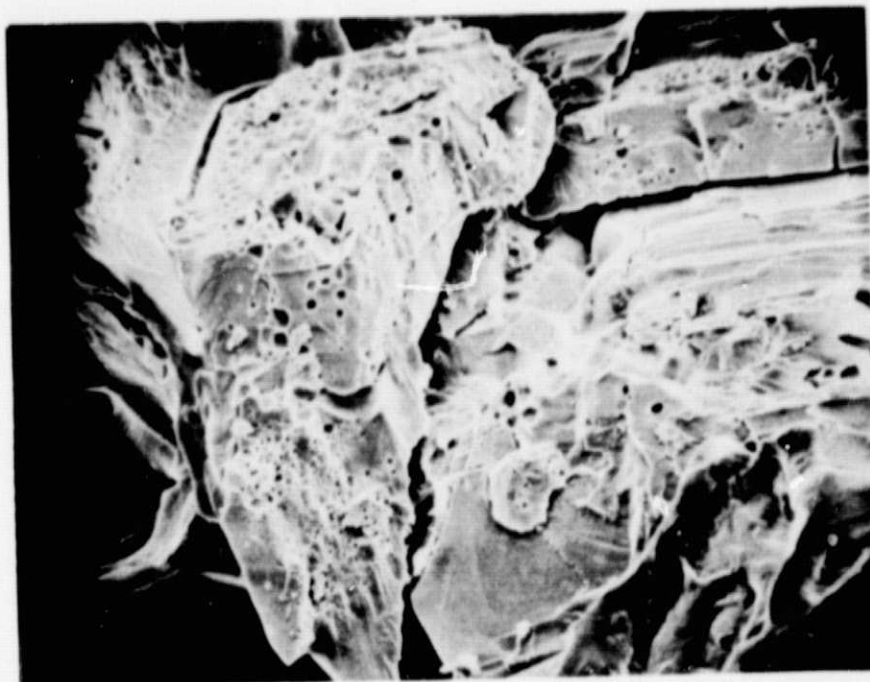
X 1.05K

1 cm ~10μ

NAS1-2852

135°C

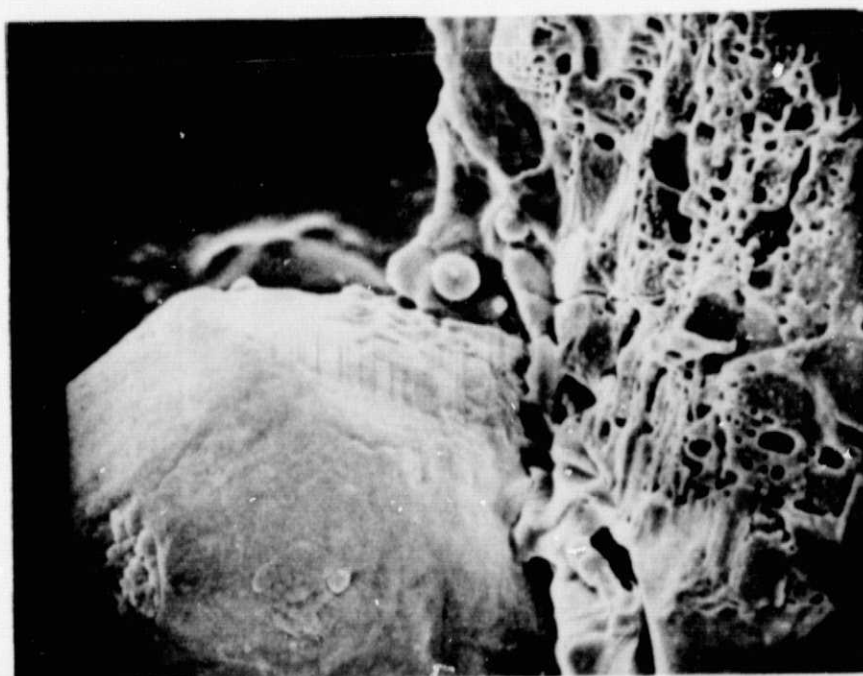
4.1 psi



X 560

1 cm ~20μ

NAS1-2909 135°C 4.1 psi

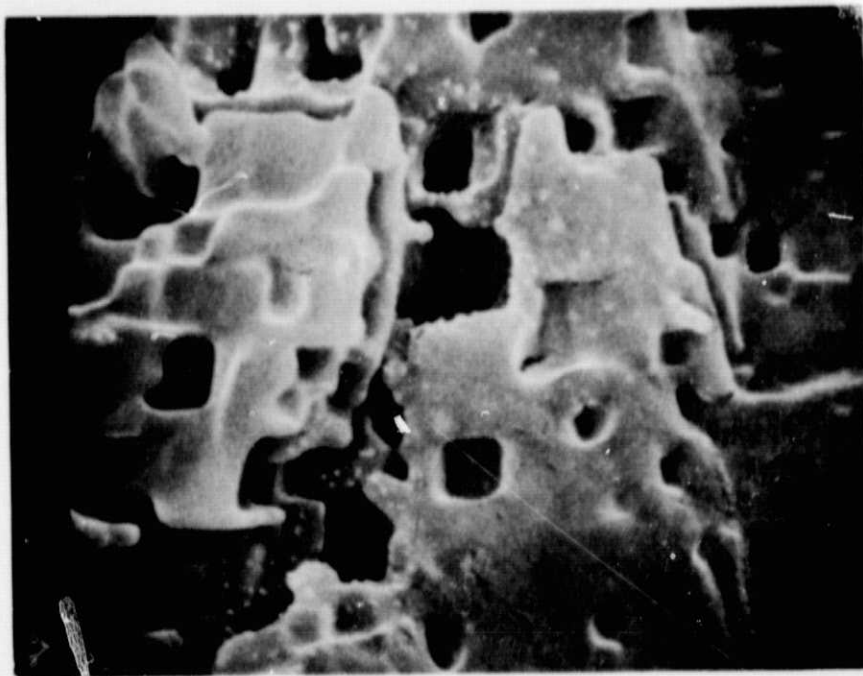


X 1.1K

1 cm ~10μ

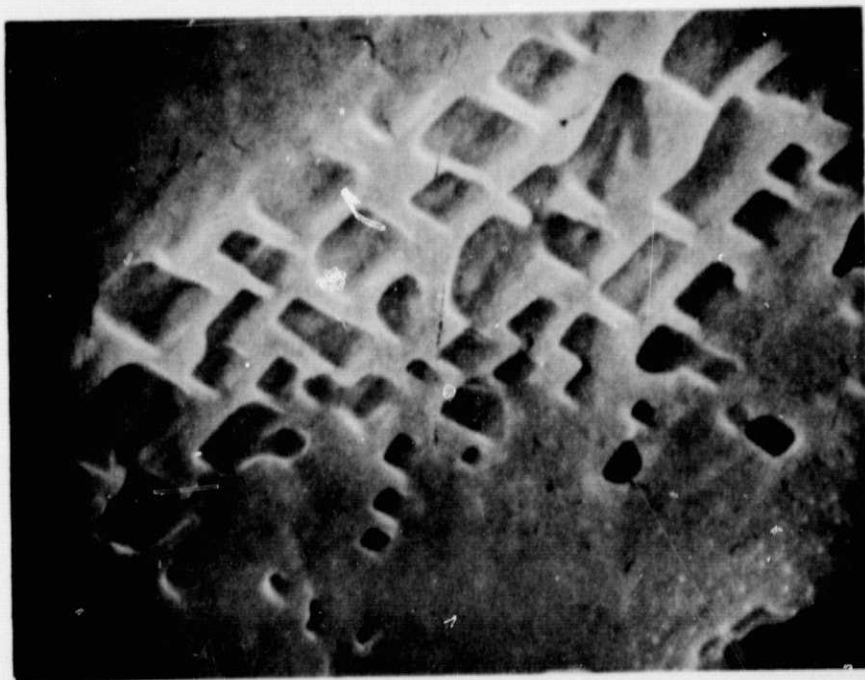
NAS1-2912 135°C 4.1 psi





X 5.6K

1 cm  $\sim 2\mu$



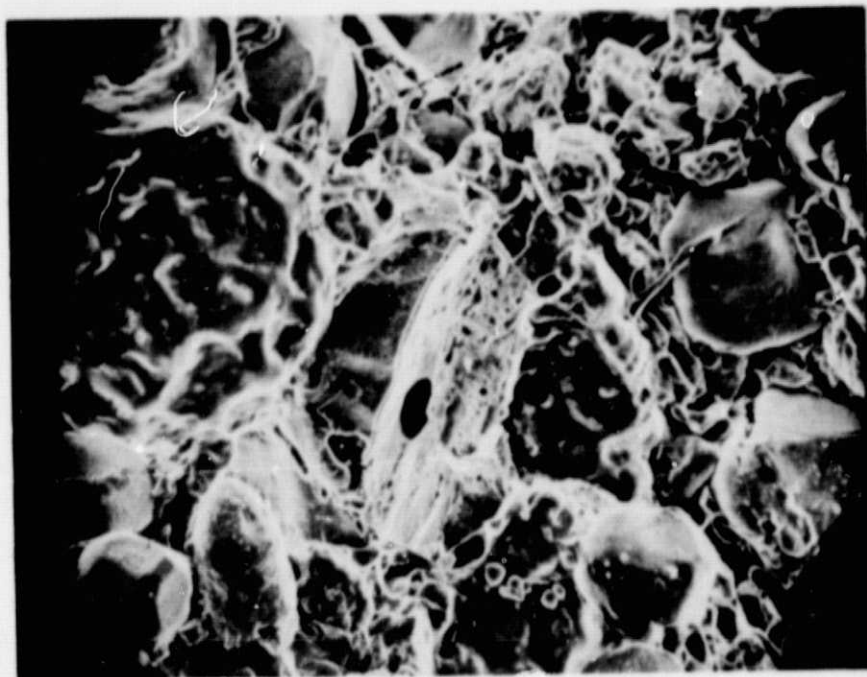
NAS1-2909

135°C

4.1 psi

-21-

Figure 4



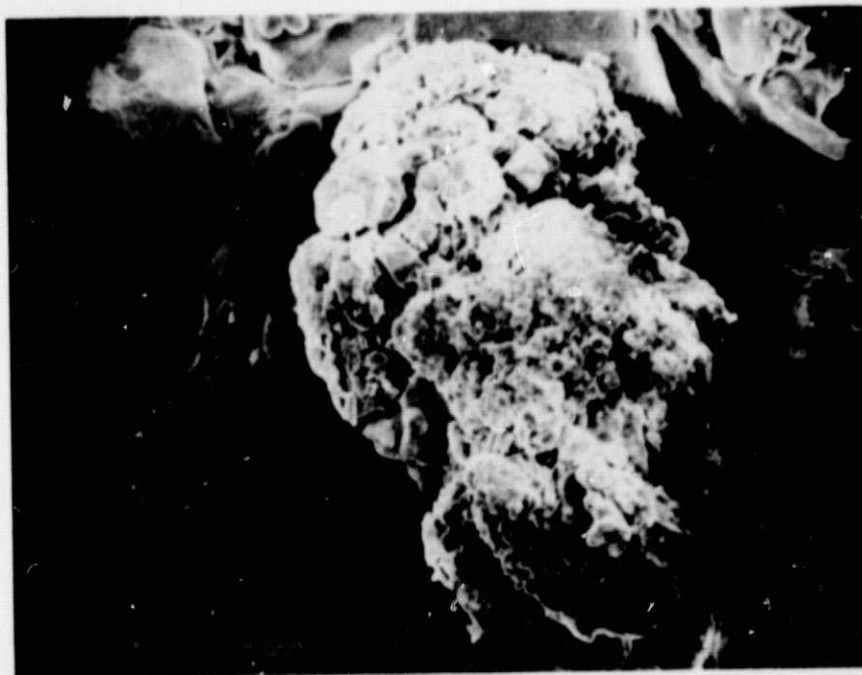
X 220

1 cm  $\approx$  50 $\mu$

NAS1-2912

135°C

4.1 psi



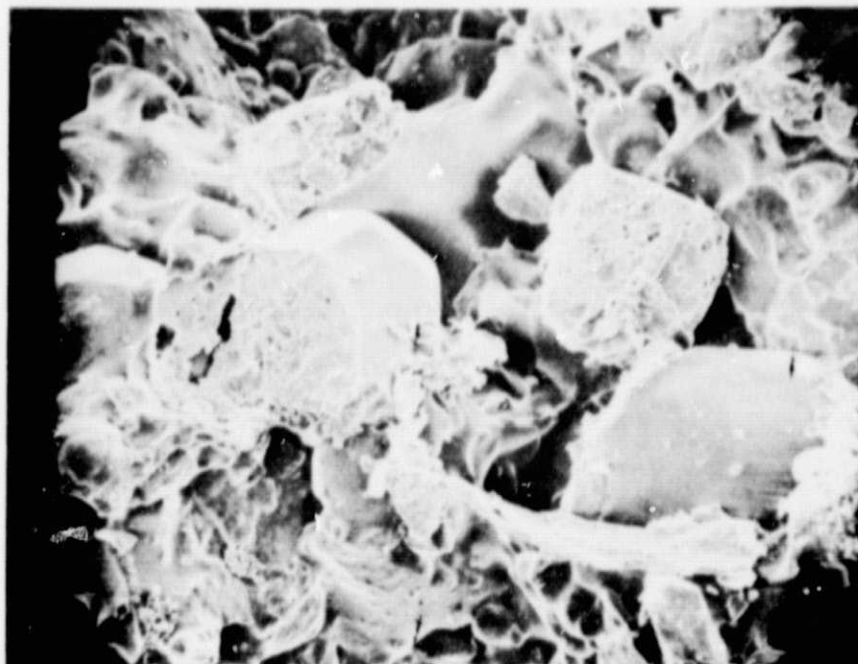
X 525

1 cm  $\approx$  20 $\mu$

NAS1-2854

135°C

4.1 psi



X 215

1 cm  $\approx$  50 $\mu$

NAS1-2912  
(ClO<sub>3</sub>)

170°C

4.1 psi



X 1.15k

1 cm  $\approx$  10 $\mu$

NAS1-2912  
(ClO<sub>3</sub>)

100°C

8.7 psi



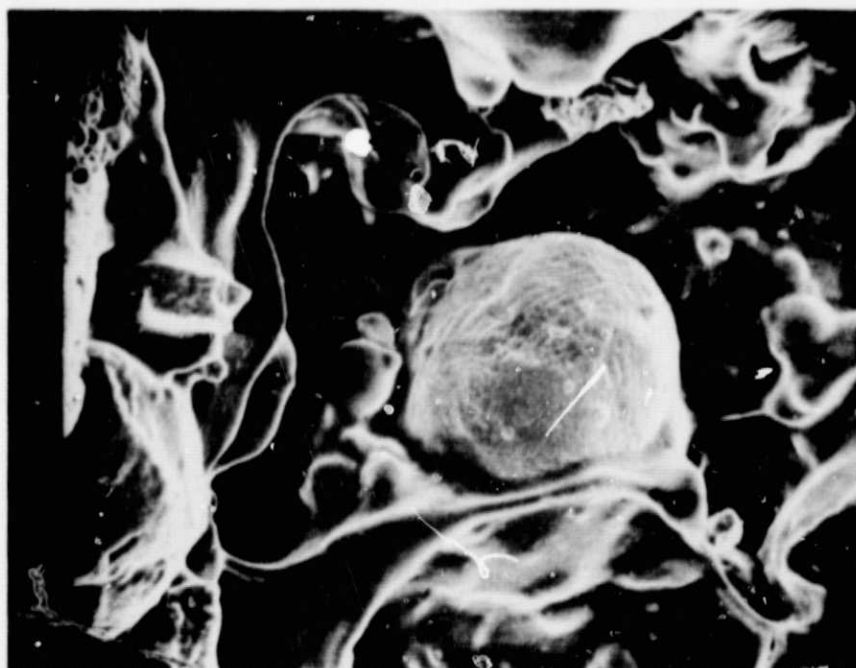
X 270

1 cm ~50 $\mu$

NAS1-2854  
(ClO<sub>3</sub>)

170°C

8.7 psi



X 550

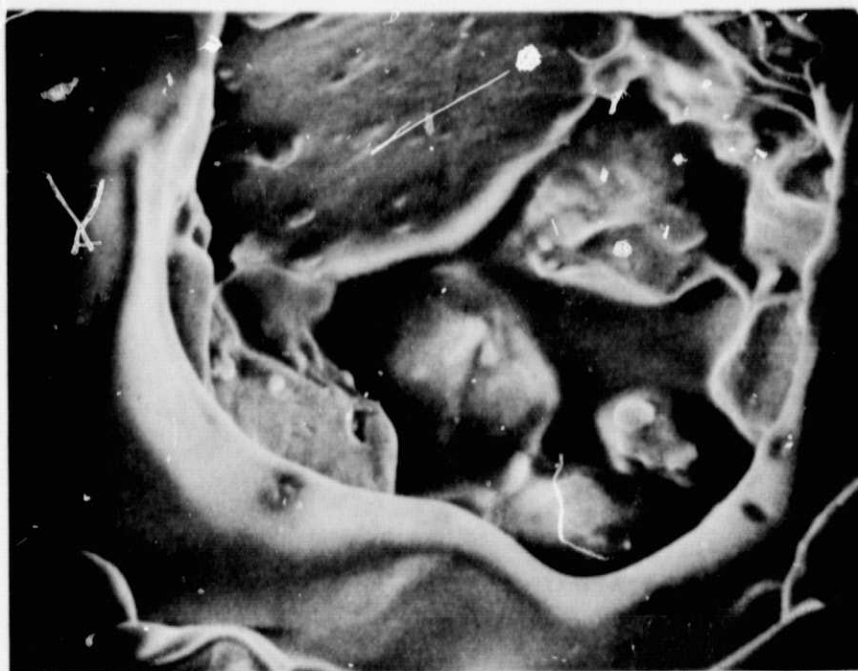
1 cm ~20 $\mu$

NAS1-2855  
(Pure AP)

170°C

4.1 psi





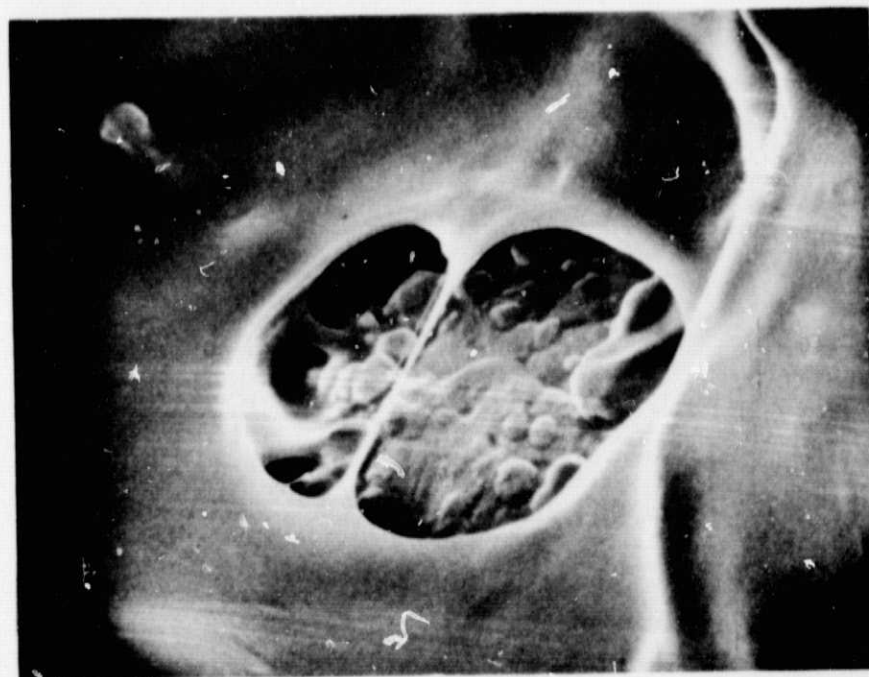
X = 1.1k

1 cm  $\sim 10\mu$

NAS1-2912  
(ClO<sub>3</sub>)

135°C

8.7 psi



X = 2.2k

1 cm  $\sim 5\mu$

NAG1-2912  
(ClO<sub>3</sub>)

135°C

8.7 psi



X 600

1 cm  $\sim 20\mu$

NAS1-2908  
( $\text{PO}_4$ )

100°C

8.7 psi



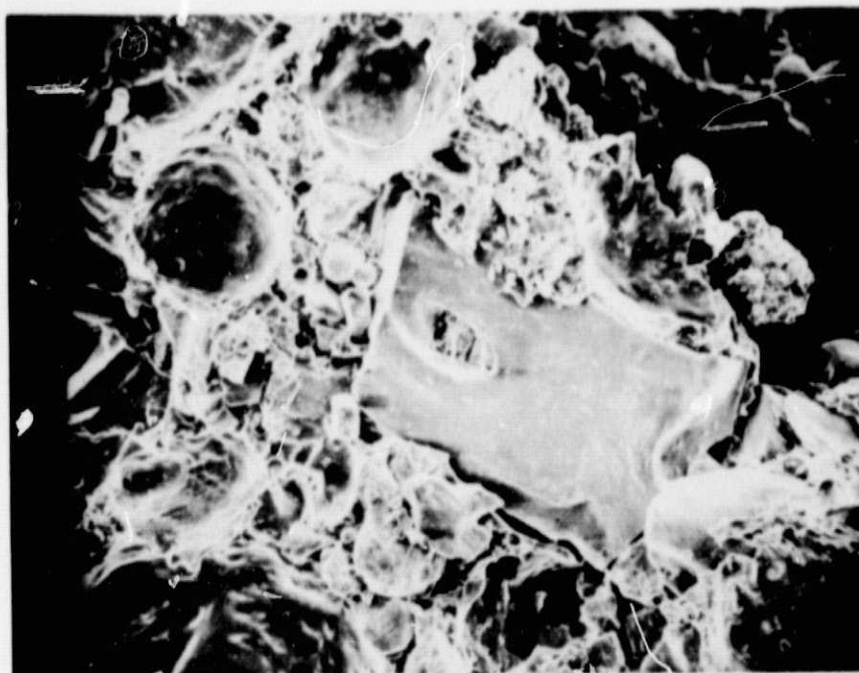
X 6.0K

1 cm  $\sim 2\mu$

NAS1-2908  
( $\text{PO}_4$ )

100°C

8.7 psi



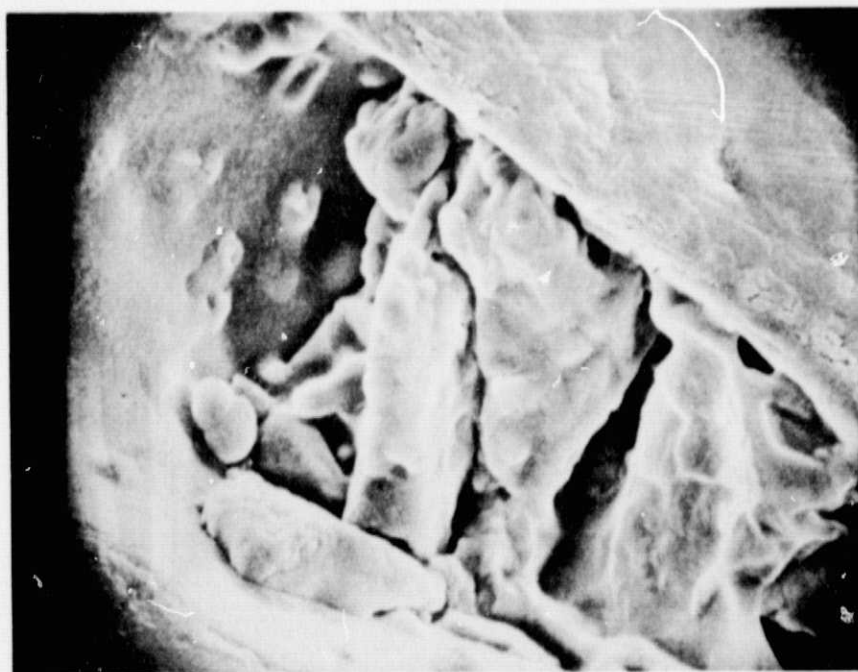
X 220

1 cm  $\sim 50\mu$

NAS1-2911A  
( $\text{PO}_4$ )

135°C

4.1 psi



X 2.2K

1 cm  $\sim 5\mu$

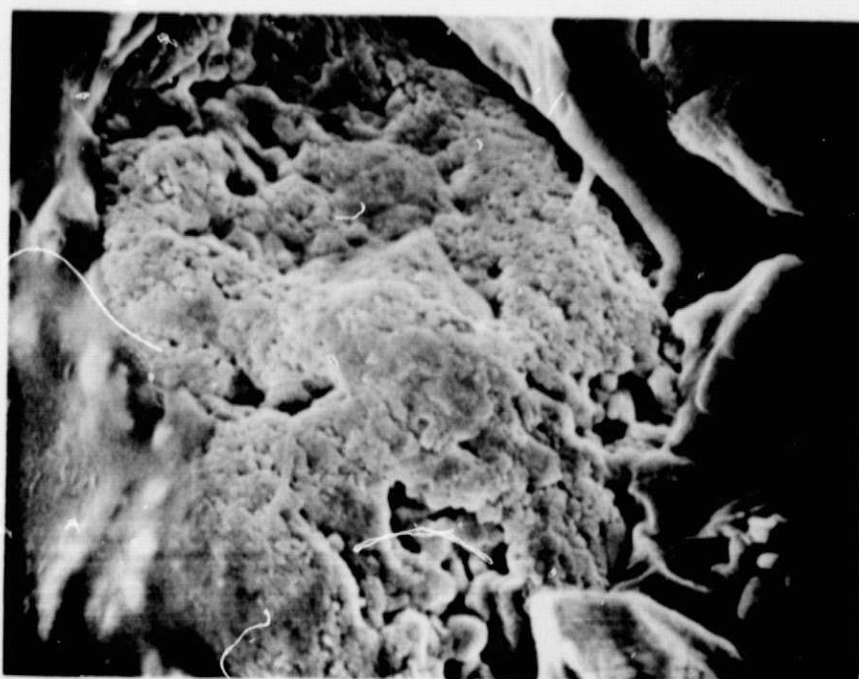
NAS1-2911  
( $\text{PO}_4$ )

135°C

4.1 psi

-27-

Figure 10



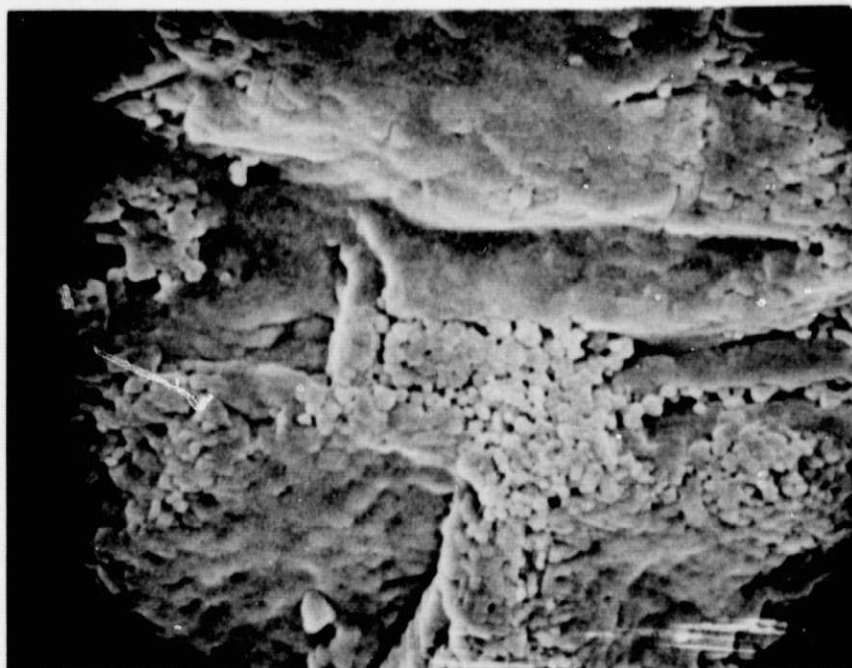
X 2.2K

1 cm  $\sim 5\mu$

NAS1-2908  
( $\text{PO}_4$ )

135°F

4.1 psi



X 2.2K

1 cm  $\sim 5\mu$

NAS1-2910  
( $\text{ASO}_4$ )

135°C

4.1 psi





X 510

1 cm  $\sim 20\mu$

NAS1-2909  
( $\text{ClO}_3$ )

100°C

8.7 psi



X = 10.1K

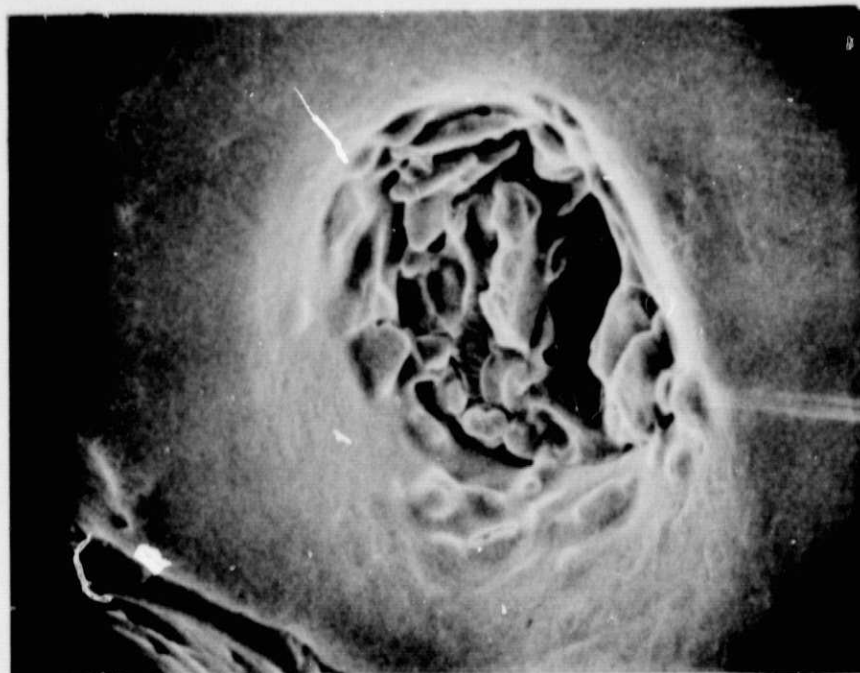
1 cm  $\sim 1\mu$

NAS1-2855  
(pure AP)

100°C

4.1 psi

Figure 12



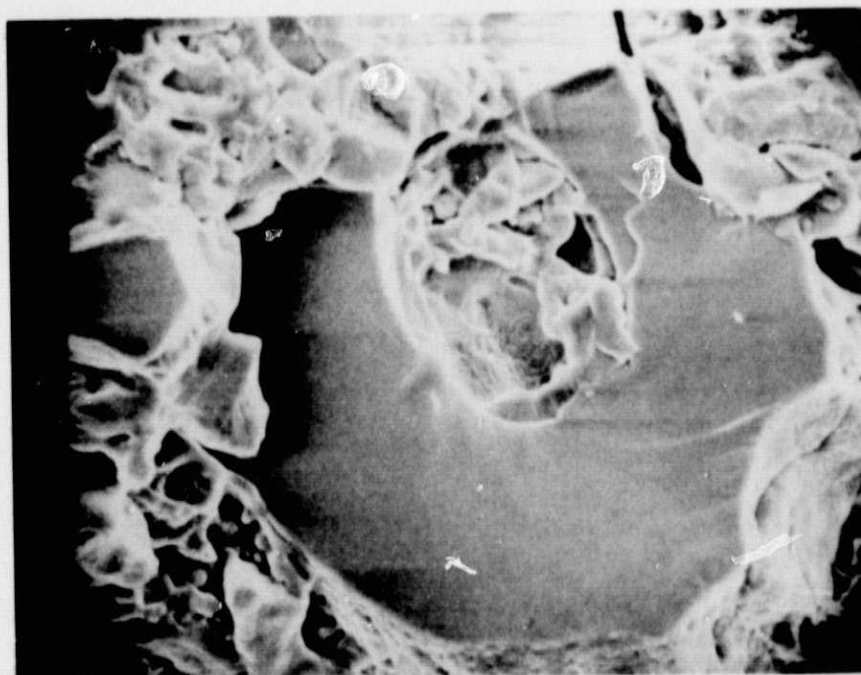
X = 1.1K

1 cm ~10 $\mu$

NAS1-2009  
(ClO<sub>3</sub>)

170°C

8.7 psi



X = 1.1K

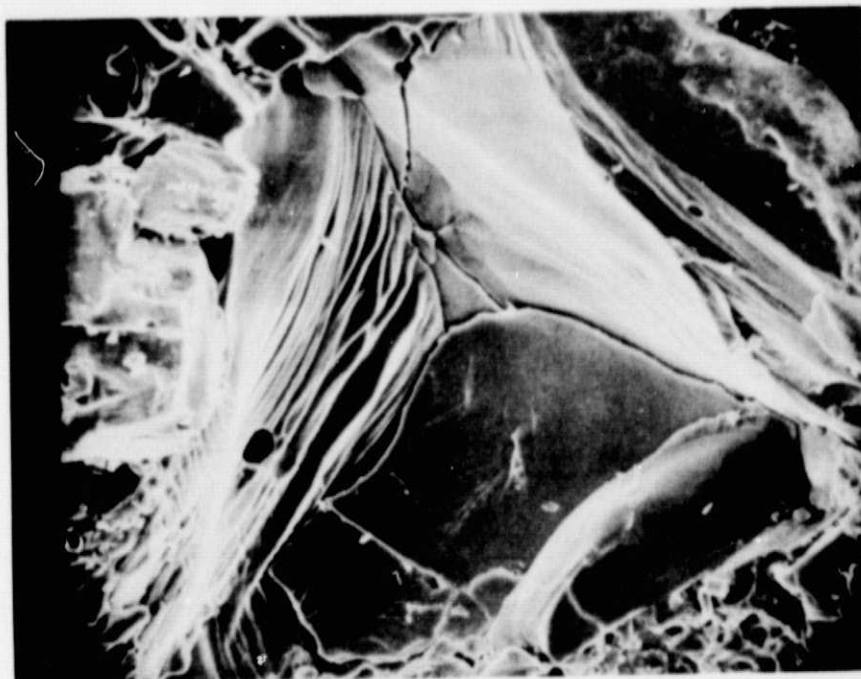
1 cm ~10 $\mu$

NAS1-2853

135°C

8.7 psi

Figure 13



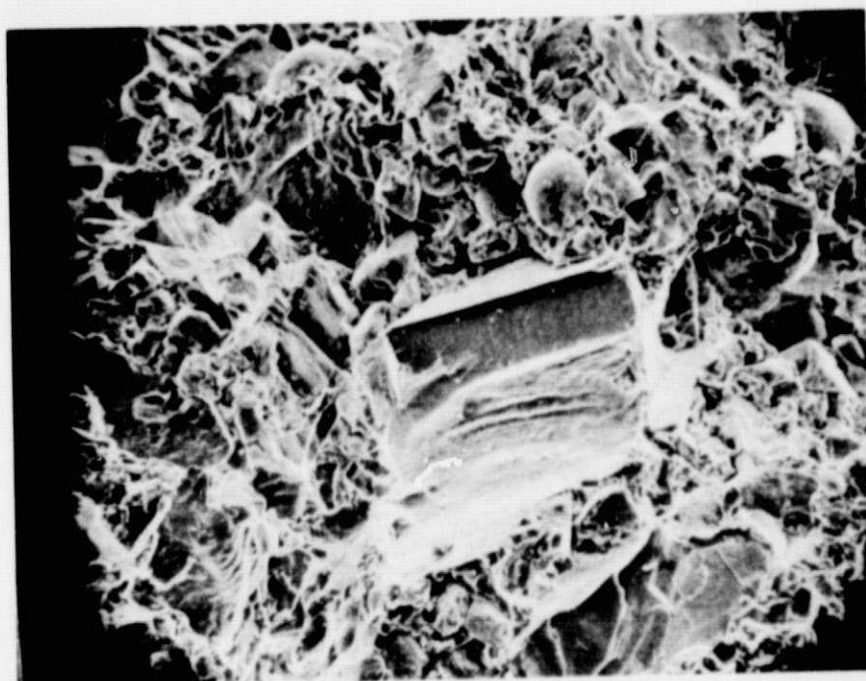
X 500

1 cm  $\sim 20\mu$

NAS1-2855

100°C

8.7 psi



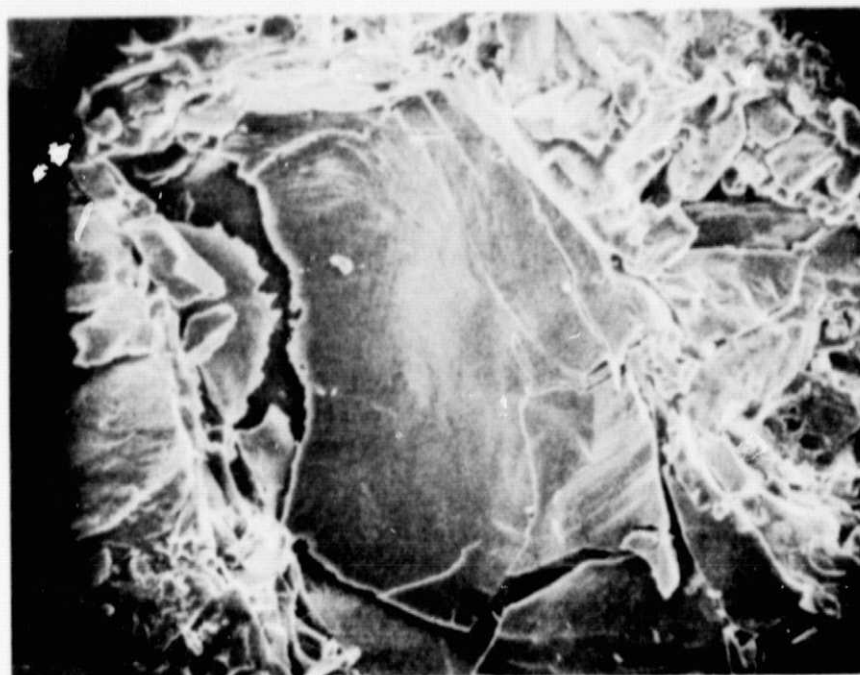
X 225

1 cm  $\sim 50\mu$

NAS1-2853

135°C

4.1 psi



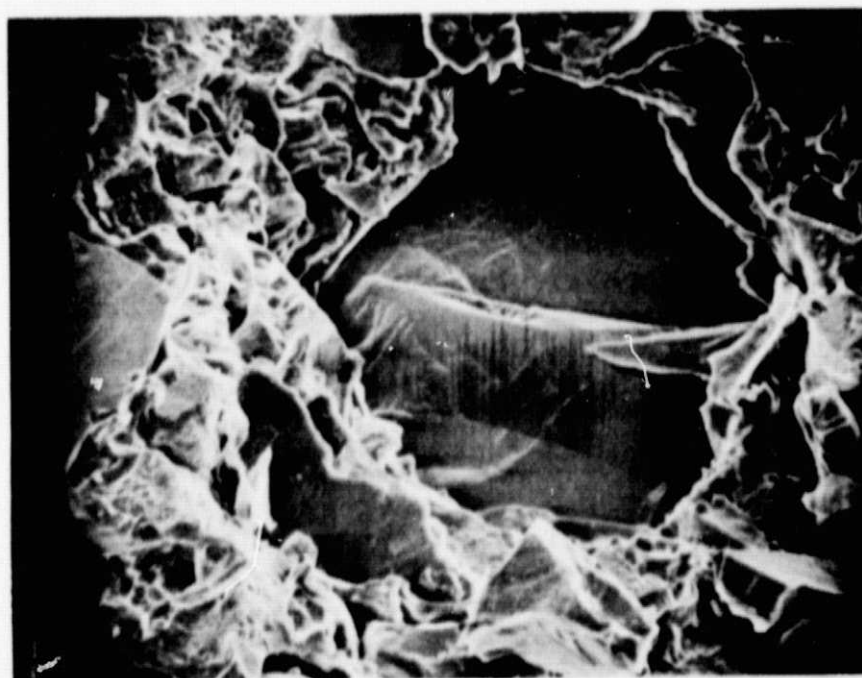
X 540

1 cm  $\sim 20\mu$

NAS1-2853

135°C

8.7 psi



X 500

1 cm  $\sim 20\mu$

NAS1-2855

135°C

4.1 psi





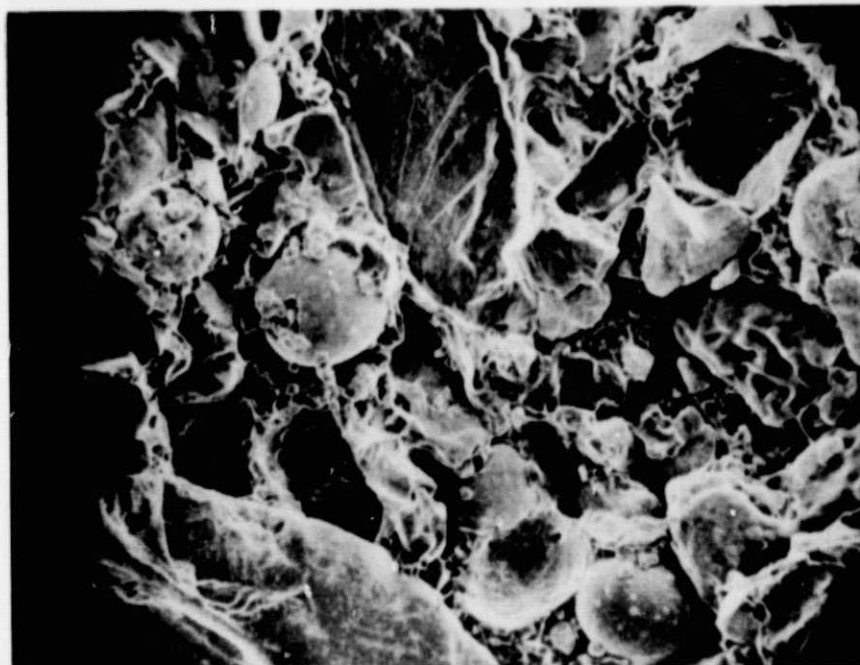
X 210

1 cm  $\sim 50\mu$

NAS1-2853

100°C

8.7 psi



X 220

1 cm  $\sim 50\mu$

NAS1-2913

135°C

8.7 psi



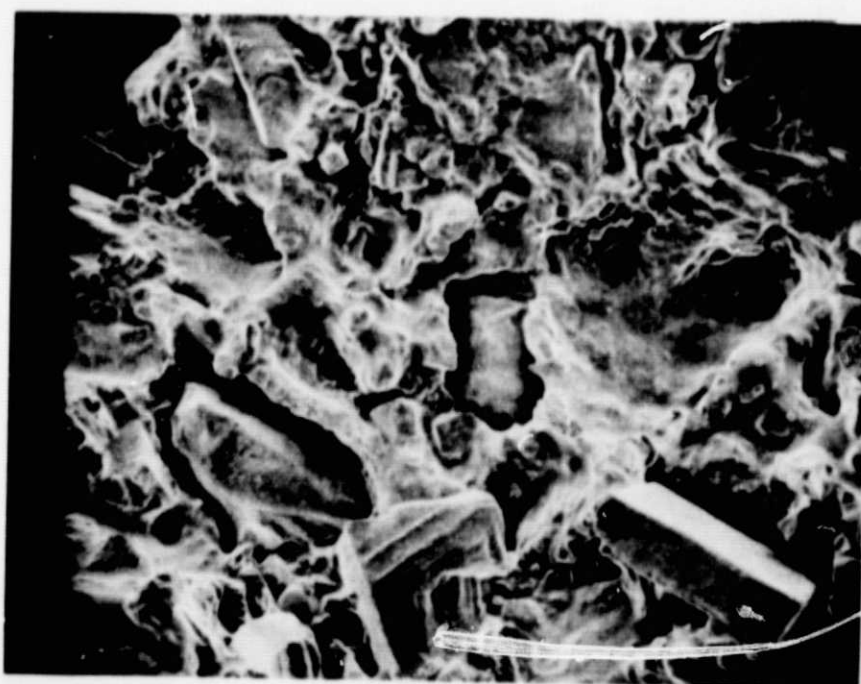
X = 2.3K

1 cm ~5 $\mu$

NAS1-2853  
(PO<sub>4</sub>)

Control

0



X = 115

1 cm ~100 $\mu$

NAS1-2853  
(PO<sub>4</sub>)

135°C

8.7 psi